



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF CHEMICAL SAFETY
AND POLLUTION PREVENTION

August 7, 2013

MEMORANDUM:

SUBJECT: Review of MRID 49190801 "The Quantification and Characterization of Silver Released from Textiles Treated with NSPW-L30SS: As a Result of Simulated Laundering Conditions", Study Number 110112.0001 Revision 2, 04-30-2013

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MRID No.: 49019201, 49045301, 49190801	40 CFR: NA

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Attached is a review of MRID 49190801. This study is the second revision of the original studies (MRIDs 49019201 and 49045301) which were revised to correct typographical errors and clarify the procedures used for sample preparation and analysis. In addition, the two reports (MRIDs 49019201 and 49045301) were combined into one report (MRID 49190801).

1.0 Introduction

This study was submitted by NanoSilva, LLC in support of the textile use for their proposed product NanoSilva NSPW-L30SS. This product is proposed for use as a preservative in synthetic textiles such as polyester. It will be applied as a master batch marketed under the brand name Polyguard. A master batch is a plastic pellet formulation that is added to the plastic polymer mixture prior to the production of fibers. The proposed application rate in the final treated article is 10 to 30 ppm silver. The study consisted of a washing machine test where fabric samples were washed in a simulated washer according to the ISO test method for colorfastness. The washing fluid consisted of tap water and detergent to simulate laundering conditions that result in down the drain environmental exposures and artificial saliva to simulate saliva contact exposures that occur when toddlers suck or mouth treated textiles.

2.0 Materials Tested

This study was conducted with polyethylene terephthalate (PET) fabric samples that had been manufactured to nominally contain 36 ppm silver. This concentration was obtained by using a PET polymer extrusion mix which contained 85 percent untreated PET and 15 percent master batch. The master batch contained 98 percent untreated PET and 2 percent Nanosilva NSPW-L30 which contains 1.19 percent silver (all percentages are by weight). The analytical concentration (listed as the theoretical concentration in the report) was 26.2 ppm based on previous analysis of the silver content and recovery rate of 95.1 percent for NSPW-L30SS and 77.4 percent for the master batch.

The treated fabric samples were taken from extra-large black knit sport shirts. Control samples were taken from a two meter long piece of untreated white fabric composed of 100% PET. The fabric samples used for the laundering test were cut to 10 x 20 cm and were not hemmed. These samples had an average weight of 2.75 grams (n=3). The fabric samples for the saliva test were cut slightly larger (10 x 22 cm) and they were hemmed to minimize the fraying that was observed during the laundering test. These samples had an average weight of 3.73 grams (n=3).

3.0 Testing Methods

The test method was modeled after the ISO 105-C06 test method "Colour fastness to domestic and commercial laundering" that was used in Geranio et al. (2009) and Lorenz et al. (2012). The ISO test method uses steel balls in a simulated washing machine. The ISO method was modified for this study to include the use of plastic balls instead of steel balls to eliminate the possibility of silver contamination from the steel balls. Also the fabric samples were doubled in size to 8 x 20 cm and the amount of washing solution was correspondingly increased to 150 ml.

The washing solution for the laundering test consisted of 4 grams per liter of ECE detergent in distilled water at pH 10.6. The solution was added to one of three separate stainless steel containers and preheated to 40 degrees C. After preheating, one treated textile sample was added to each container and washed for 45 minutes at 40 degrees C. The sample was then removed

from the container and wrung out by hand into the container and then the contents of the container were poured into an HDPE bottle. The sample, still wet, was placed into a new stainless steel container and rinsed with 20 ml of water for 5 minutes using the washing machine. This rinse cycle was repeated using a new stainless steel container and the two collected rinsing solutions were combined and placed into an HDPE bottle. The samples were then dried and placed into plastic bags for analysis.

The washing solution for the saliva test consisted of simulated saliva that contained a mixture of sodium, potassium and ammonium salts, potassium thiocyanate, urea, sodium sulfate decahydrate, calcium chloride decahydrate, potassium phosphate and sodium bicarbonate. The samples were washed in the same manner as the laundering test samples; however, the samples were not rinsed after washing and the process was repeated three times for a total of nine samples.

4.0 Sample Preparation Methods

Wash and Rinse Solutions

The wash solution samples were filtered using separate 0.45 micron 50 mm diameter filters for each sample. The filter membranes were then cut into 3 x 3 mm pieces and were weighed out into microwave vessels and digested with 3ml HNO₃ in a CEM digester. After digestion, the sample was diluted to 10 ml with deionized water.

The filtrate from the wash solution sample was collected, placed into a sealed test tube and labeled for direct analysis.

Textiles

The textile was cut into 3 x 3 mm pieces (100 to 150 mg) and weighed out into a microwave vessel and digested with 3 ml HNO₃ in a CEM digester. After digestion the control samples were diluted to 10 ml and the treated samples were diluted to 25 ml.

5.0 Sample Analysis

The samples were analyzed with Inductively Coupled Plasma – Mass Spectrometry (ICP-MS). The instrument was calibrated with standards containing 10, 20, 50, 100 and 200 ppb silver in 2 percent nitric acid. The resulting calibration line had a correlation coefficient of greater than 0.995.

The limit of quantitation LOQ was reported to be 0.094 ppb for filtrates (i.e. liquids) and 9.4 ppb for the textiles and filters (i.e. solids). As discussed in Appendix A; however, the Agency evaluated the study data and determined that the actual LODs are 10 ppb for filtrates and 1,000 ppb for solids.

6.0 Quality Control

Quality control (QC) blank samples included the following:

- One untreated polyester fabric sample used for washing in detergent.
- Three untreated polyester fabric samples used for washing in saliva.
- One filtrate each from untreated textile wash and rinse solutions,
- One filter/residue sample each from untreated textile wash and rinse solutions
- Three filtrates each from untreated textile saliva solutions,
- Three filter/residue samples from untreated textile saliva solutions.

No silver was detected in any of these samples.

QC samples included initial calibration verification solutions (ICV) and continuing calibration verification (CCV) solutions of 100 ppb, a filter spiked with 5000 ppb silver nitrate, untreated fabric spiked with a solution of 10 ppm silver nitrate and blank solution spiked with 5000 ppb silver nitrate. The results of the ICV and CCV samples indicated an average recovery of 97.6 ppb (n=14) with a standard deviation of 3.0 ppb. Additional information regarding the ICV and CCV samples is included in Appendix A. The results of the spike samples are included in Table 1.

Table 1 – Quality Control Spiked Samples

Sample Type	Sample ID*	Flask #	Measured (ppb)	Expected (ppb)
Silver nitrate solution spike onto fabric	Textile Spike	SM 3889-3	9,600	10,000
Silver nitrate solution spike onto fabric	Textile Spike	SM 3889-4	9,800	10,000
Blank solution spiked with silver nitrate – before filtration	9a	SM 3389-2	4,877	5,000
Blank solution spiked with silver nitrate – after filtration	9b	SM 3889-1	4,885	5,000

*The results of the above samples are listed on pages 116 to 118 of the study report.

7.0 Results

Silver Content of Textiles

The silver content of the textiles was analyzed in duplicate for each sample before and after washing. A listing of the results is included in Table 2 for the samples washed in detergent and in Table 3 for the samples washed in saliva.

The silver concentration in the textiles prior to washing in detergent ranged from 23,637 to 24,931 ppb with a mean of 24,198 ppb (i.e. 24.2 ppm) which was similar to what was expected (26.2 ppm) given the application rate and recovery rates observed in previous studies. The average concentration of silver in the textile after washing ranged from 21,594 ppb to 24,047 ppb with a mean of 23,182 ppb (23.1 ppm). The change in the silver content of the textile samples ranged from a loss of 0.61% to a loss of -8.6% with a mean loss of 4.3%. The study author noted that some of this loss might have been due to fiber release from the edges of the samples which were not hemmed.

The silver concentration in the textiles prior to washing in saliva ranged from 24,072 to 26,109 ppb with a mean of 25,413 ppb (i.e. 25.4 ppm). The average concentration of silver in the textile after washing ranged from 24,065 ppb to 26,742 ppb with a mean of 25,314 ppb (25.3 ppm). The change in the silver content of the textile samples ranged from a loss of 6.8 % to a gain of 5.9% with a mean of -0.34%. These samples were hemmed.

Silver Content of the Laundering Solution and Rinse Water

The results for the filter and filtrate samples of the wash water are given in Table 4 and they indicate that 1.6 percent of the silver in the textile was released. All of the results were less than the LODs and values of one half the LOD were used in accordance with OPP Policy (US EPA, 2000) to calculate the amount of silver released.

Silver Content of Saliva Wash Solution

The results for the filter and filtrate samples of the saliva are given in Table 5 and they indicate that 0.9 percent of the silver was released. All of the results were less than the LODs and one half the LOD was used in the calculations.

8.0 Conclusions

The study indicates that 1.6 percent of the silver in NanoSilva treated polyester fabric is released during washing in detergent and 0.9 percent of the silver is released during washing in simulated saliva. The study is acceptable and can be used for risk assessment.

References

- Geranio, 2009. The Behavior of Silver Nanoparticles during Washing. Geranio, L., Heuberger, M., Nowack, B., *Environmental Science and Technology* 43:8113-8118, September, 2009.
- Lorenz, C., Windler, L., von Goetz, N. et al. 2012. Characterization of silver release from commercially available functional (nano) textiles. *Chemosphere* 89:817-824.
- US EPA, 2000. Assigning Values to Nondetected/Non-Quantified Pesticide Residues in Human Health Food Exposure Assessments, Office of Pesticide Programs, U.S. Environmental Protection Agency, March 23, 2000

Table 2 – Silver Content of Textile Samples Washed in Detergent										
Before Washing (Addendum 4)					After Washing (Addendum 6)				Change in Silver Content	
Sample ID	Sample #	Flask #	Silver in Textile (ug/kg)	Silver in Textile (ug) ^A	Sample #	Flask #	Silver in Textile (ug/kg)	Silver in Textile (ug) ^A	ug ^B	Percent ^C
3092012-A1	1	M0544-1	24,199	66.6	2	M3889-35	24,197	66.5		
Duplicate		M0544-2	23,851	65.6		M3889-36	23,614	64.9		
Average			24,025	66.1			23,906	65.7	0.40	-0.61
3092012-A2	2	M0544-7	24,158	66.4	3	M3889-37	23,793	65.4		
Duplicate		M0544-8	25,703	70.7		M3889-38	24,301	66.8		
Average			24,931	68.6			24,047	66.1	2.5	-3.6
3092012-A3	3	M0544-13	24,076	66.2	4	M3889-40	21,594			
Duplicate		M0544-14	23,198	63.8		N/A				
Average			23,637	65.0			21,594	59.4	5.6	-8.6
Average (n=3)			24,198	66.6			23,182	63.7	2.8	-4.3

A. Silver in textile (ug) = Silver in Textile (ug/kg) * weight of textile (2.75 gm) * 0.001 gm/kg

B. Silver Released (ug) = Silver in textile before washing (ug) – Silver in textile after washing (ug)

C. Silver Released (percent) = [Silver released (ug) / Silver in textile before washing (ug)] * 100

Table 3 – Silver Content of Textile Samples Washed in Saliva Solution

Textile ID	Before Washing (Addendum 7)				After Washing (Addendum 9)				Change in Silver Content	
	Sample #	Flask#	Silver in Textile (ug/kg)	Silver in Textile ^A (ug)	Sample #	Flask #	Silver in Textile (ug/kg)	Silver in Textile (ug)	ug ^B	Percent ^C
3092012-A1-1 Duplicate Average	1	M2422-1 M2422-2	25,232 25,372 25,302	94.1 94.6 94.4	4	Mag 7 Mag 8	25,116 23,014 24,065	93.7 85.8 89.8	-4.6	-4.9
3092012-A1-2 Duplicate Average	2	M2422-3 M2422-4	26,831 26,262 26,547	100.1 98.0 99.0	5	Mag 9 Mag 10	24,834 26,327 25,581	92.6 98.2 95.4	-3.6	-3.6
3092012-A1-3 Duplicate Average	3	M2422-5 M2422-6	26,207 25,371 25,789	97.8 94.6 97.1	6	Mag 11 Mag 12	25,325 23,198 24,262	94.5 86.5 90.5	-6.6	-6.8
3092012-A2-1 Duplicate Average	4	M2422-7 M2422-8	23,178 24,967 24,073	86.5 93.1 89.8	7	Mag 13 Mag 14	24,293 26,204 25,249	90.6 97.7 94.2	+4.4	+4.9
3092012-A2-2 Duplicate Average	5	M2422-9 M2422-10	25,289 26,781 26,035	94.3 99.9 97.1	8	Mag 15 Mag 16	26,984 26,499 26,742	100.7 98.8 99.7	+2.6	+2.7
3092012-A2-3 Duplicate Average	6	M2422-11 M2422-12	25,776 23,106 24,441	96.1 86.2 91.2	9	Mag 17 Mag 18	23,758 24,840 24,299	88.6 92.7 90.6	-0.6	-0.7
3092012-A3-1 Duplicate Average	7	M2422-13 M2422-14	26,897 25,322 26,110	100.3 94.4 97.4	10	Mag 19 Mag 20	25,351 23,715 24,533	94.6 88.5 91.5	-5.9	-6.1
3092012-A3-2 Duplicate Average	8	M2422-15 M2422-16	26,278 23,628 26,391	98.0 88.1 93.1	11	Mag 21 Mag 22	26,563 26,373 26,468	99.1 98.4 98.6	+5.5	+5.9
3092012-A3-3 Duplicate Average	9	M2422-17 M2422-18	24,862 26,504 25,683	92.7 98.9 94.1	12	Mag 23 Mag 24	26,415 26,841 26,628	98.5 100.1 99.3	+5.2	+5.5
Average (n=9)			25,597 ± 850	94.8 ± 3.1			25,314 ± 1,090	94.4 ± 4.0	-0.4 ± 4.9	-0.34 ± 5.2

A. Silver in textile (ug) = Silver in Textile (ug/kg) * weight of textile (3.73 gm) * 0.001 gm/kg

B. Silver Released (ug) = Silver in textile before washing (ug) – Silver in textile after washing (ug)

C. Silver Released (percent) = [Silver released (ug) / Silver in textile before washing (ug)] * 100

Table 4 – Amount of Silver Released following Washing in Detergent												
Sample I.D.	Silver in Textile Before Washing ^A	Water (LOD = 10 ug/liter)				Filter/Residue (LOD = 1000 ug/kg)					Silver Released	
		Sample #	Flask #	Silver (ug/L)	Silver ^{B,C} (ug)	Sample #	Flask #	Silver (ug/kg)	Filter (gm)	Silver ^{B, D} (ug)	ug ^E	Percent ^F
Wash Water (Addendum 5)												
3092012-A1	66.1 ug	2a	3889-5	<LOD	0.75	2c	M3889-7	<LOD	0.10	0.05	0.80	
			3889-6	<LOD	0.75		M3889-8	<LOD	0.10	0.05	0.80	
3092012-A2	68.6 ug	3a	3889-9	<LOD	0.75	3c	M3889-11	<LOD	0.10	0.05	0.80	
			3889-10	<LOD	0.75		M3889-12	<LOD	0.10	0.05	0.80	
3092012-A3	65.0 ug	4a	3889-13	<LOD	0.75	4c	M3889-15	<LOD	0.10	0.05	0.80	
			3889-14	<LOD	0.75		M3889-16	<LOD	0.10	0.05	0.80	
Rinse Water (Addendum 5)												
3092012-A1	66.1 ug	6a	3889-21	<LOD	0.20	6c	M3889-23	<LOD	0.10	0.05	0.25	
			3889-22	<LOD	0.20		M3889-24	<LOD	0.10	0.05	0.25	
3092012-A2	68.6 ug	7a	3889-25	<LOD	0.20	7c	M3889-27	<LOD	0.10	0.05	0.25	
			3889-26	<LOD	0.20		M3889-28	<LOD	0.10	0.05	0.25	
3092012-A3	65.0 ug	8a	3889-29	<LOD	0.20	8c	M3889-31	<LOD	0.10	0.05	0.25	
			3889-30	<LOD	0.20		M3889-32	<LOD	0.10	0.05	0.25	
Total Amount of Silver Measured in Wash and Rinse Water												
3092012–A1											1.05	1.6
3092012–A2											1.05	1.5
3092012-A3											1.05	1.6
Average												1.6

A. Average of two replicate analyses as listed in Table 1 of this review.

B. Results were less than the LOD. Used LOD/2 for silver content calculations.

C. Silver in Wash Water (ug) = Wash Water Silver (ug/liter) * Flask Volume (0.15 liter for wash water samples and 0.040 liter for rinse water samples)

D. Silver in Filter/Residue (ug) = Silver in Filter/Residue (ug/kg) * Filter Weight (gm) * 0.001 kg/gm

E. Silver Released (ug) = Wash Water Silver (ug) + Filter/Residue Silver (ug)

F. Percent Silver Released = Silver Released (ug) / Silver in Fabric Samples (ug).

Table 5 – Amount of Silver Released following Washing in Saliva

Sample I.D.	Silver in Textile Before Washing ^A	Water (LOD = 10 ug/liter)				Filter/Residue (LOD = 1000 ug/kg)					Silver Released	
		Sample #	Flask #	Silver (ug/ liter)	Silver ^B (ug)	Sample #	Flask #	Silver (ug/kg)	Filter wt (gm)	Silver ^C (ug)	ug ^D	Percent ^E
Wash Water (Addendum 8)												
3092012-A1-1	94.4 ug	4a	1219-12 1219-16	<LOD <LOD <LOD	0.75	4c	M1220-7 M1220-8	<LOD <LOD <LOD	0.130 0.122	0.065 0.061 0.063	0.81	0.86
3092012-A1-2	99.0 ug	5a	1219-17 1219-18	<LOD <LOD <LOD	0.75	5c	M1220-9 M1220-10	<LOD <LOD <LOD	0.122 0.109	0.061 0.055 0.058	0.81	0.82
3092012-A1-3	97.1 ug	6a	1219-21 1219-22	<LOD <LOD <LOD	0.75	6c	M1220-11 M1220-12	<LOD <LOD <LOD	0.123 0.128	0.062 0.064 0.063	0.81	0.83
3092012-A2-1	89.8 ug	7a	1219-25 1219-26	<LOD <LOD <LOD	0.75	7c	M1220-13 M1220-14	<LOD <LOD <LOD	0.118 0.111	0.059 0.056 0.058	0.81	0.90
3092012-A2-2	97.1 ug	8a	1219-29 1219-30	<LOD <LOD <LOD	0.75	8c	M1220-15 M1220-16	<LOD <LOD <LOD	0.115 0.113	0.058 0.057 0.058	0.81	0.83
3092012-A2-3	91.2 ug	9a	1219-33 1219-34	<LOD <LOD <LOD	0.75	9c	M1220-17 M1220-18	<LOD <LOD <LOD	0.109 0.110	0.055 0.055 0.055	0.81	0.89
3092012-A3-1	97.4 ug	10a	1219-37 1219-38	<LOD <LOD <LOD	0.75	10c	M1220-19 M1220-20	<LOD <LOD <LOD	0.112 0.111	0.056 0.056 0.056	0.81	0.83
3092012-A3-2	93.1 ug	11a	1219-41 1219-42	<LOD <LOD <LOD	0.75	11c	M1220-21 M1220-22	<LOD <LOD <LOD	0.120 0.115	0.060 0.058 0.059	0.81	0.87
3092012-A3-3	94.1 ug	12a	1219-45 1219-46	<LOD <LOD <LOD	0.75	12c	M1220-23 M1220-24	<LOD <LOD <LOD	0.117 0.118	0.059 0.059 0.059	0.81	0.86
Overall Mean + SD (n=9)											0.81	0.85 + 0.029

A. Average of two replicate analyses as listed in Table 3 of this review.

B. Silver in Wash Water (ug) = Wash Water Silver (ug/liter) * Flask Volume (150 ml) * 0.001 liter/ml

C. Silver in Filter/Residue (ug) = Silver in Filter/Residue (ug/kg) * Filter Weight (gm) * 0.001 kg/gm

D. Silver Released (ug) = Wash Water Silver (ug) + Filter/Residue Silver (ug)

E. Percent Silver Released = Silver Released (ug) / Silver in Fabric Samples (ug).

F. All results were less than the LOD. Used LOD/2 for silver content calculations.

Appendix A – Calculation of the Detection Limit for the NanoSilva Study: The Quantification and Characterization of Silver Released from Textiles Treated with NSPW-L30SS as a Result of Simulated Laundering Conditions

This appendix documents how the detection limit included in the Nanosilva study is not valid and calculates a recommended level of detection. These calculations are based on a review of the procedures detailed in the OPP Position Paper: Assigning Values to Non-Detected/Non-Quantified Pesticide Residues in Human Health Food Exposure Assessments (US EPA, 2000).

1. MDL of 0.0094 µg/L is Not Valid

In Section 8.1.2 of the Nanosilva Study, the method detection level (MDL) for silver is stated as 0.0094 µg/L for liquid samples and 0.94 µg/kg for solid samples. As stated in Section 7.2.2 of the Nanosilva Study, the MDL represents the minimum concentration of silver that can be identified and reported with 99% confidence that the silver concentration is greater than zero, which is consistent with the definition at 40 CFR 136. In Section 8.1.3 of the Nanosilva Study, it is stated that the limit of quantitation (LOQ) is 0.094 µg/L for liquid samples and 9.4 µg/kg for solid samples. The LOQ is defined in Section 7.2.3 as being 10 times the MDL, which was previously communicated to Nanosilva in a phone call on January 25, 2013.

The MDL and LOQ described above differ from the detection limits described in the OPP position paper on assigning values to non-detected results for pesticide residues in human health food exposure assessments (US EPA, 2000). In this position paper, EPA introduced the term limit of detection (LOD) as:

Limit of Detection (LOD) is defined as the lowest concentration that can be determined to be statistically different from a blank. This concentration is recommended to be three standard deviations above the measured average difference between the sample and blank signals which corresponds to the 99% confidence level.

This value is calculated based on the expected instrument response for calibration samples. The Inductively Coupled Plasma Mass Spectrometer (ICP-MS) responses to silver calibration samples analyzed on December 1, 2012 (page 59 of the Nanosilva Study) are shown in Table 1.

Table 1 – Estimated LOD and LOQ Based on Calibration Results from 12/01/2012				
Concentration (µg/L)	ICP-MS Response (CPS)	Expected CPS	(CPS – Expected CPS)	(CPS – Expected CPS)^2
0	697.81	-99008.43	99706.24	9941334226.02
10	354265.00	360540.16	-6275.16	39377663.10
20	805784.43	820088.75	-14304.32	204613697.89
50	2186578.84	2198734.53	-12155.69	147760813.94
100	4352969.14	4496477.49	-143508.35	20594646764.41
200	9168500.70	9091963.41	76537.29	5857956552.45
Slope	45954.86		Sum	36785689718
Intercept	-99008.43		RMSE	110733

Based on the OPP position paper, the LOD is determined from the root mean square error (RMSE) from the observed vs. expected ICP-MS response. The LOD is estimated as 3 times the RMSE or:

$$\text{Liquid LOD} = \frac{3 \times 110733 + 99008.43}{45954.86} = 9.4 \mu\text{g/L}$$

The concentration of 9.4 µg/L is the lowest concentration of silver that can be determined to be statistically different from the sample that did not contain silver (i.e., 0 µg/L). The equivalent concentration for silver in a filter sample is:

$$\text{Filter LOD } (\mu\text{g/kg}) = \frac{9.4 \mu\text{g silver}}{L \text{ water}} \frac{10 \text{ mL}}{\text{digest}} \frac{L}{1000 \text{ mL}} \frac{1000 \text{ g}}{0.1 \text{ g filter}} = 940 \mu\text{g/kg}$$

The OPP position paper also introduces the limit of quantitation (LOQ), which is defined as the level above, which quantitative results may be obtained. This is estimated as 10 times the RMSE or:

$$\text{LOQ} = \frac{10 \times 110733 + 99008.43}{45954.86} = 26.2 \mu\text{g/L}$$

According to the OPP position paper, these estimates for LOD and LOQ form the basis for determining the method detection limit and method quantitation limit which would involve analyzing seven samples containing silver at 9.4 or 26.2 µg/L, respectively. This step was not done for the Nanosilva Study because they established the MDL according to Consumer Product Safety Commission Method CPSC-CH-E1002-08.1. In the CPSC method, the instrument detection limit (IDL) is first determined from the analysis of calibration samples that do not contain silver (i.e., calibration blank). From this analysis, an IDL of 0.012 µg/L was reported (Table 8 of the Nanosilva Study). The IDL was validated by analyzing a sample with silver concentration of 0.012 µg/L seven times with a reported a MDL of 0.0094 µg/L. However, there was no comparison between the ICP-MS response for the 0.012 µg/L sample to the ICP-MS response for the 10 silver calibration blanks.

Table 2 contains the average and standard deviation for the ICP-MS response from 7 samples fortified with silver at 0.012 µg/L and the 10 calibration blank samples. This comparison shows that the ICP-MS

response for samples containing 0.012 µg/L silver were not statistically different from the 10 calibration blank samples (*students-t* = 0.28). Therefore, these results cannot be used to establish the LOD or LOQ based on the OPP position paper on assigning values to non-detected results for pesticide residues in human health food exposure assessments (US EPA, 2000).

Table 2 – ICP-MS Response for Silver Free and Silver Containing Samples			
Samples that do not contain silver (i.e., calibration blank)	ICP-MS Response (CPS)	Samples fortified with 0.012 µg/L silver	ICP-MS Response (CPS)
Blank1	768.94	R-Blank1	720.03
Blank2	727.26	R-Blank2	662.81
Blank3	916.16	R-Blank3	621.14
Blank4	773.92	R-Blank4	826.15
Blank5	852.82	R-Blank5	858.93
Blank6	763.92	R-Blank6	811.15
Blank7	542.80	R-Blank7	823.37
Blank8	415.01		
Blank9	396.13		
Blank10	616.69		
Average ± Standard Deviation	677±178		761±92

2. Determining the LOD

To establish an LOD, Nanosilva should have analyzed a sample with silver concentration of 9.4 µg/L at least seven times and reported the recovery of silver at this concentration. Since this step was not performed, EPA is establishing an LOD based on the seven calibration sample analysis results available in the Nanosilva Study. Determining the RMSE for the calibration sample analysis results reveals that the LOD ranges from 0.6 to 24.4 µg/L (Table 3) where the average LOD is 10 µg/L, which also is the lowest calibration sample concentration.

Table 3 – LOD and LOQ Determined from Eight Calibration Results		
Date of Calibration Sample Analysis	LOD µg/L)	LOQ µg/L)
12/1/2012	9.4	26.3
11/12/2012	0.6	4.8
11/6/2012	3.7	12.5
11/20/2012	3.3	12.6
12/20/2013	11.6	32.5
12/21/2012	24.4	65.9
12/21/2012	16.4	45.2
Average (µg/L)	10	29
Concentration for solids samples (µg/kg)	1000	2900

Although no independent samples with concentration of 10 µg/L were analyzed to validate the LOD of 10 µg/L, independently prepared calibration-check samples with concentration of 100 µg/L were

analyzed. Table 4 shows that the analysis of the 100 µg/L samples had recoveries between 93.6 and 102.7%, which are well within the goal of 70 to 110% according to the OPP position paper. Based on the strength of the recovery for the 100 µg/L calibration check samples, EPA is setting the LOD as 10 µg/L for liquid samples and 1000 µg/kg for solids samples. In accordance with the OPP position paper, EPA will replace any silver concentration that is below 10 µg/L with the value of 5 µg/L and any solids concentration of less than 1000 with the value of 500 µg/kg.

Table 4 – Analysis of Calibration Check Samples			
Date of Analysis	Sample Name	Concentration (µg/L)	Recovery (%)
11/12/2012	CCV	101.5	101.5
11/12/2012	ICV	102.7	102.7
11/20/2012	CCV1	100.7	100.7
11/20/2012	CCV4	93.6	93.6
11/20/2012	CCV2	95.7	95.7
12/18/2012	ICV	95.0	95.0
12/18/2012	CCV	95.3	95.3
12/18/2012	CCV2	93.9	93.9
12/20/2012	CCV2	100.4	100.4
12/20/2012	CCV3	99.4	99.4
12/20/2012	CCV4	98.9	98.9
12/21/2012	ICV	94.9	94.9
12/21/2012	CCV1	97.7	97.7
12/21/2012	CCV2	97.1	97.1
Average ± standard deviation		97.6 ± 3.0	97.6